Key Engineering Materials

Volume I

Current State of the Art on Novel Materials

Editors
Devrim Balköse, PhD
Daniel Horak, PhD
Ladislav Šoltés, PhD

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CHAPTER 6

KEY ELEMENTS ON SURFACE PROPERTIES OF POLYIMIDE COPOLYMERS

IGOR NOVÁK, PETER JURKOVIČ, JAN MATYAŠOVSKÝ, PETR SYSEL, MILENA ŠPIRKOVÁ, and LADISLAV ŠOLTES

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6.1 INTRODUCTION

Several sorts of block polyimide based copolymers, namely poly(imide-co-siloxane) (PIS) block copolymers containing siloxane blocks in their polymer backbone have been investigated. In comparison with pure polyimides the PIS block copolymers possess some improvements, for example, enhanced solubility, low moisture sorption, and their surface reaches the higher degree of hydrophobicity already at low content of polysiloxane (PSI) in PIS copolymer. This kind of the block copolymers are used as high-performance adhesives and coatings. The surface as well as adhesive properties of PIS block copolymers depends on the content and length of siloxane blocks. The surface properties of PIS block copolymers are strongly influenced by enrichment of the surface with siloxane-based segments. Micro phase separation of PIS block copolymers occurs due to the dissimilarity between the chemical structures of siloxane and imide blocks even at relatively low lengths of the blocks. The surface analysis of PIS block copolymers using various methods of investigation ,for example, contact angle measurements, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), and X-ray photoelectron spectroscopy (XPS), was performed, and the strength of the adhesive joint to more polar polymer was studied. The surface and adhesive properties are discussed in view of the varied composition of PIS block copolymers.

The polyimides present an important class of polymers, necessary in microelectronics, printed circuits construction, and aerospace investigation, mainly because their high thermal stability and good dielectric properties [1-4]. The PIS block copolymers containing siloxane blocks in their polymer backbone have been investigated [5, 6]. In comparison with pure polyimides the PIS block copolymers possess some improvements, for example, enhanced solubility, low moisture sorption, and their surface reaches the higher degree of hydrophobicity already at low content of PSI in PIS copolymer. This kind of the block copolymers are used as high-performance adhesives and coatings. The surface as well as adhesive properties of PIS block copolymers depends on the content and length of siloxane blocks. The surface properties of PIS block copolymers are strongly influenced by enrichment of the surface with siloxane segments [7]. The micro phase separation of PIS block copolymers occurs due to the dissimilarity between the chemical structures of both siloxane, and imide blocks.

6.2 EXPERIMENTAL

The 2-aminoterminated ODPA-BIS P polyimides with controlled molecular weight were synthesized by solution imidization (first step in NMP at room temperature for 24 hr, second step in NMP–BCB mixture at 180°C). The number-average molecular weights of products were in the range M_n = 2000–18,000 g/mol (by ^{1}H NMR spectroscopy). The surface morphology (height image) and local surface heterogeneities (phase image) were measured by AFM. All the measurements were performed under ambient conditions using a commercial atomic force microscope (NanoScope™ Dimension IIIa, MultiMode Digital Instruments, USA) equipped with the PPP-NCLR tapping-mode probe (Nanosensors™ Switzerland; spring constant 39 N/m, resonant

frequency 160 kHz). The surface energy of PIS block copolymer was determined via measurements of contact angles of a set of testing liquids (that is re-distilled water, ethylene glycol, formamide, methylene iodide, and 1-bromo naphthalene) using surface energy evaluation (SEE) system completed with a web camera (Masaryk University, Czech Republic) and necessary PC software. The drop of the testing liquid (V = 3 µl) was placed with a micropipette (0–5 µl, Biohit, Finland) on the polymer surface, and a contact angle of the testing liquid was measured. The peel strength of adhesive joint (P_{peel}) to polyacrylate was measured by 90° peeling of adhesive joint using universal testing machine Instron 4301 (Instron, England) with 100 N measuring cell. The adhesive joints for peel tests were fixed in aluminum peeling circle.

6.3 DISCUSSION AND RESULTS

The AFM measurements of the PIS copolymers are shown in Figure 1. Its measurements of the surface topography (height image) and tip-sample interaction (phase image) of the samples containing 0–33 wt% of siloxane monomer revealed differences in both characteristics. Only characteristic samples, that is 0, 10, 20, and 33 wt% of siloxane are shown in the Figure 1, sample containing 30 wt% of siloxane is very similar in height and phase images to the sample with 33 wt% siloxane.

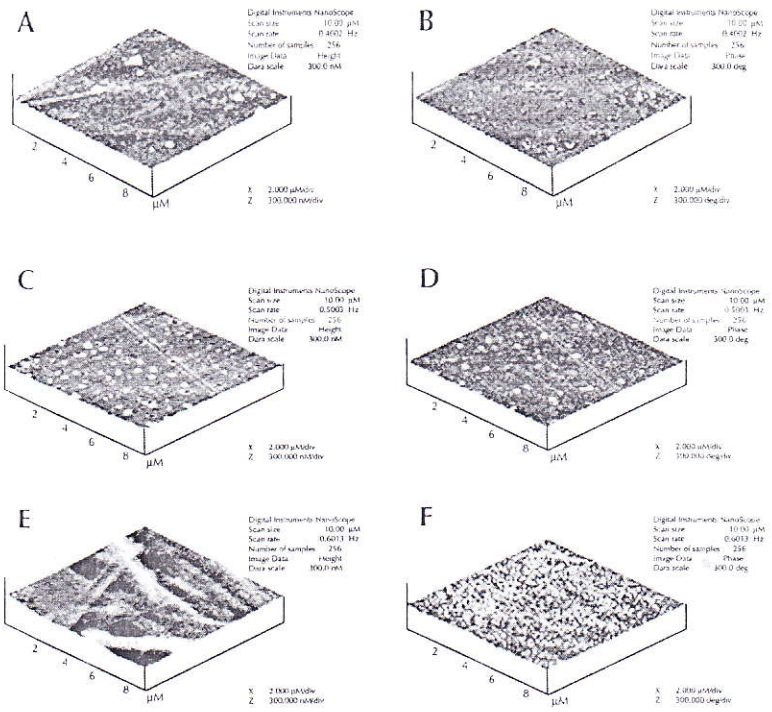

FIGURE 1 *(Continued)*

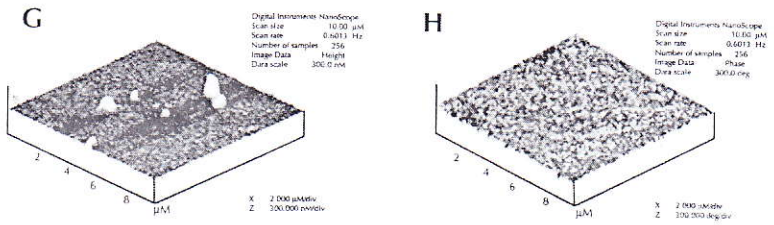

FIGURE 1 AFM images of PIS block copolymers films—pure polyimide (A, B), 10 wt% of siloxane (C, D), 20 wt% of siloxane (E, F), and 33 wt% of siloxane (G, H) Height images (A, C, E, G), and phase (B, D, F, H) images, respectively.

The comparison of height images—samples containing 20% (Figure 1 (E)) and 30% (not shown in figure) have rugged and funicular surface relief. On the other hand, surfaces of pure polyimide (Figure 1 (A)), 10% copolymer (Figure 1 (C)) and 33% copolymer (Figure 1 (D)) contain individual formations on the surfaces –"hills" of different size and height (tens–hundreds nm) and furthermore holes (tens of nm size) on 10% sample. Moreover, funicular formations are shadowed also in the Figure 1 (A) and Figure 1 (C). The comparison of phase images—Figure 1 (B) versus Figure 1 (D), and Figure 1 (F) versus Figure 1 (H) exhibit mutually similar relief. If compared the phase images with the relevant topography images, that is Figure 1 (A) versus Figure 1 (C) and Figure 1 (E) versus Figure 1 (G), it is evident while height images are similar for first couple as well, significant differences for second couple exist.

Figure 2 shows the contact angles of re-distilled water deposited on PIS block copolymer surface versus content of siloxane in copolymer. The contact angles of water by Figure 2 increased by growth of siloxane content and/or Si/N ratio in copolymer. The contact angles of PIS block copolymer increase from 76° for pure polyimide, to 95° for 10% of siloxane in copolymer up to 102° for 30% of siloxane in copolymer. Micro phase separation in PIS block copolymer occurs even at relatively low block lengths due to dissimilarity between the chemical structures of the siloxane, and imide blocks.

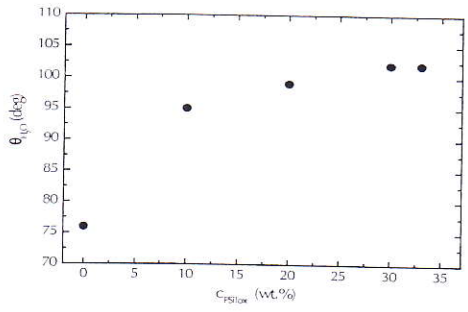

FIGURE 2 Contact angles of water versus siloxane content in PIS block copolymer.

The dependencies of the surface energy and its polar component of PIS block copolymer determined by Owens-Wendt-Rabel-Kaelble (OWRK) method [7] versus content of siloxane in copolymer are shown in Figure 3. The surface energy of PIS block copolymer decreases significantly with the concentration of siloxane from 46.0 mJ.m^{-2} (pure polyimide) to 34.2 mJ.m^{-2} (10% of siloxane), and to 30.2 mJ.m^{-2} (30% of siloxane). The polar component of the surface energy reached the value 22.4 mJ.m^{-2} (pure polyimide), which decreases with content of siloxane in PIS copolymer to 4.6 mJ.m^{-2} (10% of siloxane) and 0.8 mJ.m^{-2} (30% of siloxane) The surface energy of pure polyimide is 46 mJ.m^{-2}, while the value of the surface energy of poly (dimethyl siloxane) is only 20.9 mJ.m^{-2}. At room temperature the siloxane molecules are above their glass temperature, their segments are capable to migrate to the polymeric surface, so making it more hydrophobic. The surface of the PSI copolymer films should be covered with PSI segments having their thickness in molecular order.

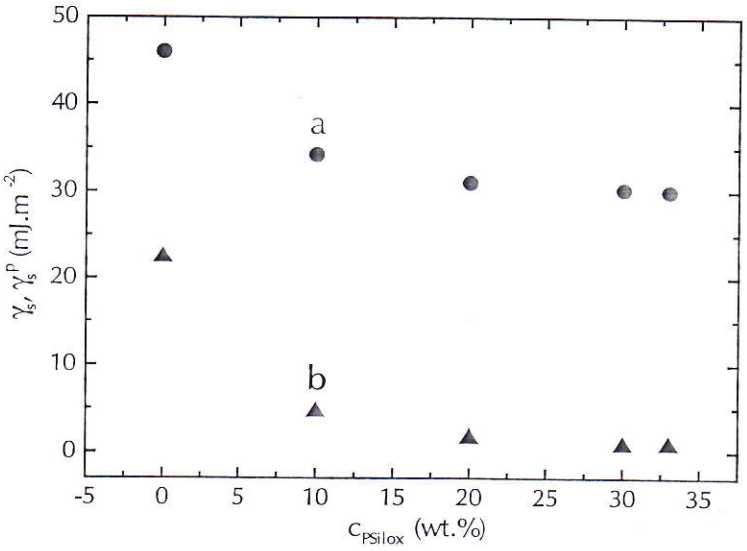

FIGURE 3 Surface energy and its polar component of PSI block copolymer versus siloxane content.

Figure 4 shows the dependence of the peel strength of adhesive joint PSI block copolymer to epoxy versus content of siloxane. It is seen that the peel strength of adhesive joint PIS copolymer-epoxy decreases with growth in siloxane content in the whole concentration range. The fact that the strength of the adhesive joints decreases with increase in siloxane content reflects the increases hydrophobicity of the polymeric surface. The peel strength of adhesive joint to epoxy adhesive diminished from 1.2 MPa (pure polyimide), to 1.05 MPa (10% of siloxane), and to 0.65 MPa (30% of siloxane). This decrease of peel strength of adhesive joint is relatively steady for all

investigated content of siloxane in block copolymer. Comparing polyimide with PSI block copolymer containing 30% of siloxane shows that the peel strength of adhesive joint to epoxy decreased more than two times. The presence of siloxane in PSI block copolymer caused the more hydrophobic surface of copolymer (surface energy of copolymer containing 10% of siloxane was 34.2 $mJ.m^{-2}$).

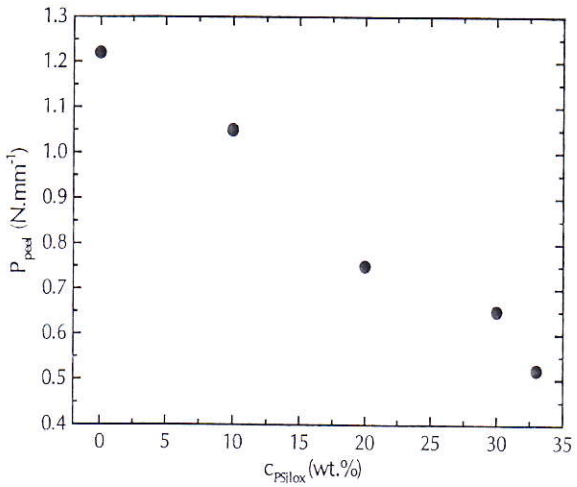

FIGURE 4 Peel strength of adhesive joint PSI block copolymer-epoxy versus concentration of siloxane.

6.4 CONCLUSION

The morphology of PIS block copolymer has been changed due segregation of siloxane segments, constitution of polyimide continuous phase in copolymer was affirmed. A significant increase of roughness of PSI copolymer surface, if the content of siloxane is growing, was observed. The values of contact angles of water extremely increased by rising of siloxane content in PSI block copolymer and at higher composition were leveled off. The content of siloxane in copolymer increased, the surface energy, and its polar component of PSI copolymer diminished, the dispersive component of the surface energy on opposite increased, and if the content of siloxane in PIS copolymer rises up, strength of adhesive joint to epoxy decreased almost linearly.

KEYWORDS

- Atomic force microscopy
- Hydrophobicity
- Poly(imide-co-siloxane)
- Siloxane
- Surface energy evaluation

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